

Ketonization of Long-Chain Esters

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Abstract

The possibility of obtaining ketones with two long carbon chains in the process of long chain esters transformation was studied. The reactions were carried out over catalyst containing Fe, Si, Cr and K oxides in a standard flow system under atmospheric pressure in temperature range of 320-400°C and at load of 1.5 h⁻¹. n-Decyl n-decylate, n-butyl n-dodecylate and methyl n-dodecylate were used as substrates.

Keywords: iron oxide catalyst, ketonization of n-decyl n-decylate, ketonization of n-butyl n-dodecylate, ketonization of methyl n-dodecylate.

Introduction

During ketonization of normal alcohols over an iron catalyst, the appearance of esters was observed in the products, especially at lower reaction temperatures [1]. This suggested the possibility of efficient transformation of esters to ketones over the catalyst, which was proved empirically [2]. Esters are subject to ketonization with higher selectivity and at lower temperature of the transformation maximum than corresponding alcohols [3]. The usage of long-chain esters as a raw material should lead to obtaining ketones with two long carbon chains without harmful by-products, which is the case in other methods of receiving long-chain ketones [4, 5].

Ketones with two long chains can be used as material for further syntheses, especially for producing surface-active agents of double lipophilic chains. The agents are highly effective at low concentration, and consequently, less harmful to the natural environment; they are susceptible to biodegradation [6, 7]. They can be obtained by reductive amination of ketones with ammonia or methylamine to amines with two long carbon chains with primary amino group at secondary carbon atom [8].

Experimental Procedure

The ketonization reactions were carried out in a standard flow system under atmospheric pressure. Fe, Si, Cr and K oxides in the molar ratio of 100 : 2 : 1 : 0.1 were the catalyst [9]. The experiments were performed at a catalyst charge of 3.0 cm³ with a flow intensity of 4.5 cm³ of liquid/h and at temperature 320-400°C. The catalyst was pre-reduced with methanol at 200°C for 1 h, then the substrate was fed. Products were identified by gas chromatography and mass spectroscopy. The gaseous products (H₂, CO and low molecular hydrocarbons) formed in studied reactions were not collected and analyzed.

n-Decyl n-decylate (containing the same number of carbon atoms at acid and alcohol sides), n-butyl n-dodecylate and methyl n-dodecylate were used as substrates.

Results and Discussion

Table 1 presents the conversions of n-decyl n-decylate and yields of the main liquid products. The reaction pro-

Table 1. The results of *n*-decyl *n*-decylate transformation.

| Reaction temperature [°C] | Conversion [%] | Total yield of <i>n</i> -decene and <i>n</i> -decane [%] | Total yield of <i>n</i> -dodecanal and <i>n</i> -dodecanol-1 [%] | Yield of 10-nonyldecanone [%] | Other liquid products [%] |
|---------------------------|----------------|----------------------------------------------------------|------------------------------------------------------------------|-------------------------------|---------------------------|
| 323 | 5.5 | 1.0 | 2.7 | – | 1.3 |
| 337 | 13.0 | 3.0 | 4.5 | 2.0 | 2.0 |
| 345 | 22.0 | 6.0 | 6.0 | 5.0 | 2.5 |
| 354 | 34.2 | 9.8 | 7.5 | 9.9 | 3.1 |
| 367 | 61.3 | 11.3 | 10.1 | 31.9 | 3.5 |
| 380 | 92.7 | 14.1 | 2.1 | 67.0 | 4.0 |
| 390 | 97.0 | 19.0 | – | 66.1 | 4.9 |
| 395 | 98.0 | 21.0 | – | 63.5 | 5.5 |
| 400 | 99.8 | 25.4 | – | 59.0 | 6.0 |

Table 2. The results of *n*-butyl *n*-dodecylate transformation.

| Reaction temperature [°C] | Conversion [%] | Total yield of <i>n</i> -dodecene and <i>n</i> -dodecane [%] | Total yield of <i>n</i> -dodecanal and <i>n</i> -dodecanol-1 [%] | Yield of 12-tricosanone [%] | Yield of 4-pentadecanone [%] | Yield of 4-heptanone [%] | Others liquid products [%] |
|---------------------------|----------------|--------------------------------------------------------------|------------------------------------------------------------------|-----------------------------|------------------------------|--------------------------|----------------------------|
| 323 | 5.0 | 1.0 | 2.0 | – | – | – | 1.0 |
| 337 | 11.5 | 4.0 | 3.0 | – | – | – | 2.0 |
| 345 | 18.5 | 6.0 | 3.5 | 1.0 | 1.0 | 1.0 | 3.0 |
| 354 | 30.0 | 9.0 | 5.5 | 2.2 | 3.6 | 2.2 | 2.0 |
| 367 | 55.2 | 12.0 | 9.2 | 7.1 | 10.7 | 7.2 | 3.0 |
| 380 | 85.8 | 14.5 | 11.3 | 14.3 | 21.4 | 14.3 | 4.2 |
| 390 | 93.0 | 14.9 | – | 19.2 | 28.7 | 19.0 | 5.2 |
| 395 | 94.8 | 16.1 | – | 18.8 | 27.8 | 18.2 | 5.9 |
| 400 | 96.6 | 16.1 | – | 17.3 | 25.1 | 16.2 | 5.6 |

Table 3. The results of methyl *n*-dodecylate transformation.

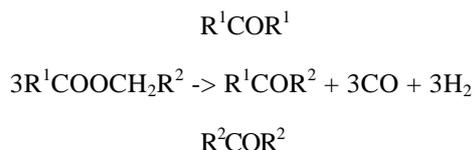
| Reaction temperature [°C] | Conversion [%] | Total yield of <i>n</i> -dodecene and <i>n</i> -dodecane [%] | Total yield of <i>n</i> -dodecanal and <i>n</i> -dodecanol-1 [%] | Yield of 12-tricosanone [%] | Other liquid products [%] |
|---------------------------|----------------|--------------------------------------------------------------|------------------------------------------------------------------|-----------------------------|---------------------------|
| 323 | 3.0 | 0.5 | 1.0 | – | 1.0 |
| 337 | 6.0 | 2.0 | 2.0 | – | 1.0 |
| 345 | 12.5 | 4.0 | 3.0 | – | 2.0 |
| 354 | 22.2 | 6.0 | 5.7 | 4.0 | 2.0 |
| 367 | 50.6 | 10.6 | 8.0 | 20.0 | 3.0 |
| 380 | 80.6 | 12.1 | 12.5 | 40.5 | 4.2 |
| 390 | 89.3 | 13.4 | 3.1 | 56.1 | 4.6 |
| 395 | 93.0 | 14.6 | – | 58.3 | 5.3 |
| 400 | 96.6 | 16.1 | – | 58.6 | 5.6 |

ceeds in accordance with the equation:



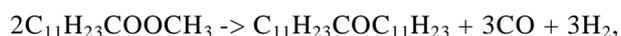
The side products are hydrocarbons C_{10} and at lower temperatures, in accordance with the reaction mechanism [10], aldehyde C_{10} and alcohol C_{10} .

In case of esters differing in the number of carbon atoms at acid and alcohol sides there is formed a mixture of symmetrical and asymmetrical ketones:



The results of n-butyl n-dodecylate ketonization are presented in Table 2.

The conversion of methyl n-dodecylate proceeds according to the equation:



because of the secondary condensation of $C_nH_{23}CHO$ and $C_{11}H_{23}CH_2OH$, which are formed at an intermediate stage and the degradation of Ci group. As a result, only one ketone $C_{11}H_{23}COC_{23}H_{23}$ is obtained but with higher yield than its yield from n-butyl w-dodecylate.

Nevertheless, the total efficiency of ketones is higher with n-butyl n-dodecylate (66.9% at 390°C). The same liquid flow intensity of both esters corresponds to higher molar load in case of methyl n-dodecylate. It is probably one of the causes of the difference. Moreover, according to the equation, in methyl n-dodecylate conversion there appear relatively more gases, which correspond to more intense linear flows, and thus, shorter contact time. Theoretically n-decyl n-decylate should convert to $C_{11}H_{23}COC_{23}H_{23}$ ketone with relatively highest efficiency, as no mixed ketones or C_1 groups transforming into CO and H_2 are obtained. It should be noted, however, that the assumptions are supported also by considerably lower molar load at the same liquid flow intensity.

Because of high melting points of the products, the ketonization of long-chain esters is possible also with the use of diluent, e.g. toluene, which is neutral in the process, facilitates receiving products, and is easy to separate. Proper experiments were carried out with positive results. There is also a possibility of usage of higher alcohols as a diluent and, at the same time, co-condensatory agent. In the case of n-butyl n-dodecylate the resultant heptanone-4 behaves as a diluent.

Thus, it is an effective method of obtaining ketones with two long carbon chains over heterogeneous catalyst. The optimization of the process parameters means an improvement in results, while the theoretical efficiency of the process is high as for the economy of the amount of material atoms entering into the final product. On the other hand, the reductive amination of two-long-chain ketones is a method which technically enables obtaining required amines. The amination of methyl esters of fatty

acids, which means the elimination of the ketonization stage, does not lead to amines containing two long carbon chains.

Summary

The possibility of obtaining ketones with two long carbon chains in the process of long chain esters conversion over an iron catalyst was described. The differences in the efficiency of resultant ketones can be ascribed to molar loads and overall conversion mechanism [10]. The ketonization of symmetrical «-decyl «-decylate is the most efficient, but it is not an easily accessible substrate. A potential source of the material are methyl, and possibly, butyl esters which are obtained in the transesterification process of technical fats, which was elaborated in Poland [11, 12]. From the ecological prospective the solution is worth considering for the management of those harmful and renewable wastes.

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